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도시계획학석사 학위논문

**Comparison of DOC Properties in Extracted
Soil Solution between *Cryptomeria japonica*
and *Quercus acutissima***

삼나무 숲과 상수리나무 숲 토양 추출수의 특성 비교

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Abstract

Dissolved organic carbon (DOC) in soils can be leached to streams and rivers where it can be decomposed to CO₂, affecting the local and global carbon cycle. I investigated the biogeochemical properties of soil DOC under the two contrasting tree species using extraction experiments in laboratory scale. Soil samples were collected at soil depths of 0-10, 10-30, and 30-50 cm under Japanese cedar (*Cryptomeria japonica*) and sawtooth oak (*Quercus acutissima*) stands in Bukmoon-gol, Beakwoon Mountain, Jeollanam-do, South Korea. The extraction of soil organic carbon (SOC) was conducted using deionized water (DI) under three extraction conditions (EC). The concentrations of DOC and major cations, optical properties of DOC, and $\Delta^{14}\text{C}$ -DOC were analyzed. The results showed that the concentrations of extracted DOC ([DOC]) and cations ([Cations]) were higher under *Cryptomeria japonica* than under *Quercus acutissima*, while SOC contents were not significantly different between the two tree species. These results suggest that hydrophilicity of soil DOC is more influential to DOC extraction than the quantity of SOC. The ratio of [DOC] to [Cations] did not vary between tree species and ECs, supporting the usage of [DOC]/[Cations] value as an indicator of flow pathway in mineral soils. $\Delta^{14}\text{C}$ -DOC under *Cryptomeria japonica* was 70.49, 35.08, and 4.15‰ at 0-10, 10-30, and 30-50 cm depth, respectively, while 44.9, 41.29, and -53.25‰ of $\Delta^{14}\text{C}$ -DOC were measured at each soil depth under *Quercus acutissima*. This suggests that ¹⁴C-depleted DOC would be predominantly exist in soils deeper than 50 cm. Relatively higher $\Delta^{14}\text{C}$ -DOC compared to $\Delta^{14}\text{C}$ -SOC indicates that soil DOC is primarily derived from hydrophilic, exchangeable fraction of SOC, not from SOC strongly bonded to mineral soils.

Keyword: Dissolved organic carbon, soil solution, forest, tree species, radiocarbon

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1. Introduction

Dissolved organic carbon (DOC) is a relatively mobile portion of organic carbon in natural systems. DOC engages in various ecological reactions and processes, such as soil formation (Kalbitz et al. 2000, Lundstrom et al. 2000) and the transport of nutrients and pollutants from soil to surface waters (Magee et al. 1991, Qualls and Haines 1991, Kalbitz et al. 2000, Delle Site 2001, Kaiser 2001). DOC is introduced into soil through microbial decomposition, throughfall, litter leaching, or root exudates (Bolan et al. 2011). Some portion of DOC is removed from soil by respiration, transported to streams by lateral flow, or leached to groundwater, while remaining DOC can persist in soils by binding to minerals (Kalbitz et al. 2000, Bolan et al. 2011).

Soil DOC can affect the carbon cycle when exported to streams, where DOC is decomposed to CO₂ or transported to the ocean (Cole et al. 2007, Aufdenkampe et al. 2011, Regnier et al. 2013). The emission of CO₂ is more prominent in headwater streams (Butman and Raymond 2011, Hotchkiss et al. 2015, Marx et al. 2017) due to large input of allochthonous carbon that can be transformed into gaseous carbon by microbial activities (Battin et al. 2008) or photodegradation (Cory et al. 2015). Therefore, knowing the quantity and the sources of soil DOC in headwater catchments is necessary to understand the significance of streams in the global carbon cycle.

Typically, the ¹⁴C-age of riverine DOC is known to be modern because it is mostly originated from vegetation or organic compounds in soils (Kalbitz et al. 2000, Raymond and Bauer 2001). However, the preliminary study of this topic, conducted in Beakwoon Mountain in Gwanyang, Jeollanam-do, South Korea, observed DOC aged up to 620±25 years in the headwater during dry periods (Lee et al., *in preparation*). Different from previous studies that predominantly observed ¹⁴C-enriched

DOC in headwaters (Table 1), the finding from this preliminary study suggests that ^{14}C -depleted DOC can be leached from mineral soils to streams in temperate forests. However, the ^{14}C -ages of soil DOC has been rarely studied.

Many studies have focused on the controlling factors that can influence leaching of soil DOC. Forest types can influence soil DOC as shown in the studies that observed larger DOC concentration in coniferous stands than in broadleaf stands (Currie et al. 1996, Borken et al. 2011, Fröberg et al. 2011). Climatic factors also play an important role in the export of soil DOC. Mostly, DOC is exported through surface runoff during high-flow periods, such as rainfall and snowmelt (Lambert et al. 2013, Raymond et al. 2016). However, much less information is available on the factors affecting the ^{14}C -age of soil DOC in forested ecosystems. Most studies only observed vertical gradient of radiocarbon contents (Nakanishi et al. 2012, Elizabeth Corbett et al. 2013) or calculated the turnover rate of organic carbon in soils (Michalzik et al. 2003, Tipping et al. 2011). Some studies measured $\Delta^{14}\text{C}$ of soil DOC to study other carbonic matters, such as stream DOC, CO_2 , and soil organic carbon (SOC), not to study the properties of soil DOC (Leith et al. 2014, Benk et al. 2018).

The objectives of this research are (1) to compare the biogeochemical properties of DI-extracted DOC of soils under the two contrasting tree species using three extracting conditions, and (2) to investigate whether mineral soil horizons can produce ^{14}C -depleted DOC. The biogeochemical properties of water extractable DOC of soils under *Cryptomeria japonica* and *Quercus acutissima* were analyzed including the concentrations of extracted DOC and major cations, optical properties of DOC, and $\Delta^{14}\text{C}$ -DOC. This study is the first attempt to investigate $\Delta^{14}\text{C}$ -DOC extracted from soils in the Republic of Korea to clarify the role of tree species on $\Delta^{14}\text{C}$ of soil DOC.

Table 1. Studies on $\Delta^{14}\text{C}$ -DOC of headwater streams in forested watersheds.

Location	Sampling year	Climate	Watershed Size [†] (km ²)	$\Delta^{14}\text{C}$ (‰)	References
Siksik Creek, Canada	2014	Arctic	0.94	6.4-96.4	Dean et al. (2018)
Kolyma River, Russia	2003	Boreal	NA [†]	36-150	Neff et al. (2006)
Valipuro and Suopuro, Finland	2008	Boreal	0.86-1.13	73.1-125.6	Billett et al. (2012)
Krycklan catchment, Sweden	1999, 2007	Boreal	0.47	14-116	Ledesma et al. (2015)
Degero Stormyr mire, Sweden	2015-2016	Boreal	2.7	79-118	Campeau et al. (2017)
Harp Lake basin, Canada	1997	Temperate	0.22-2	-171-190 ^{††}	Schiff et al. (1997)
Brocky Burn watershed, Scotland	1998	Temperate	1.3	24.4-56.7	Palmer et al. (2001)
Ore Mountain, Germany	2008-2010	Temperate	4-5	-40-42 ^{†††}	Tittel et al. (2013)
Chesapeake Bay, USA	2008-2009	Temperate	NA	65-114	Lu et al. (2014)

[†] NA: not available.^{††} Among 36 samples, negative $\Delta^{14}\text{C}$ of DOC was detected in five samples.^{†††} Among 12 samples, negative $\Delta^{14}\text{C}$ of DOC was detected in four samples.

2. Materials and Methods

2.1. Site description

The study site is the Bukmoon-gol forested watershed in Baekwoon Mountain, Gwangyang, Jeollanam-do, South Korea (35.0319° N, 127.6050° E) (Fig. 1). The watershed size is 0.333 km². The average depths of O horizon and A horizon are 5.9 cm and 24.1 cm (Im et al. 2007). The soils are composed of sandy loam and clay loam, and the bedrock is mostly granite and partially gneiss (Park et al. 2000). This region was reforested since 1920s, and is composed of both coniferous and deciduous trees, each accounting for about 70% and 30% of the entire watershed (Im et al. 2007). *Cryptomeria japonica* (Japanese cedar) and *Quercus acutissima* (sawtooth oak) stands in the watershed were planted in 1959 and 1926, respectively.

The region is in the temperate monsoon climate zone, which is characterized by the monsoon period in summer, and the dry period in winter. For the years from 2009 to 2018, the annual precipitation of the watershed ranged from 874 to 2162 mm, with the average annual precipitation of 1509 mm. Average summer (June-August) precipitation was 789 mm, which is approximately half of the average annual precipitation. Average temperature was around 23 °C in summer, 4 °C in winter.

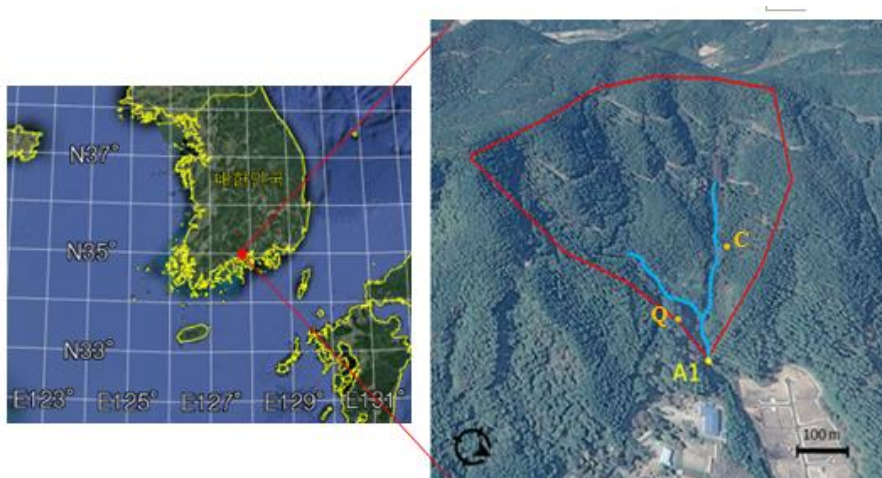


Figure 1. The location and the boundary of the forested watershed of this study. The red line indicates the boundary of the watershed. Soil samples were collected at point C (*Cryptomeria japonica* stand) and Q (*Quercus acutissima* stand). The blue line shows the stream pathway. Stream samples were collected at A1, which is the mouth of the second-order stream.

2.2. Laboratory experiments

2.2.1. Soil sampling

Soil samples were collected from mineral soil horizons under two different tree species (*Cryptomeria japonica* and *Quercus acutissima*) at three different soil depths (0-10, 10-30, 30-50 cm) from three pits (denoted as pit 1, 2, 3) on March 15, 2019. Collected soil samples were then sieved with 5.6 mm screen to remove large stones. All samples were stored in field-moist at 4 °C before soil solution extraction.

2.2.2. Soil solution extraction

I used extraction methods modified from Jones and Willett (2006) and Kalbitz et al. (2007). Soil solution was extracted with DI to measure the concentration of DOC and major ions. The following three different

extraction conditions (EC) were applied to compare how extraction conditions influence the properties of extracted DOC. I simulated the water retention time and water content in the soils as explained below.

EC1. 1:10 w/v (weight/volume) soil-to-solution ratio (20 g of soil mixed with 200 ml of DI), stirred by a glass rod for 1 minute. Short water retention time with high water content.

EC2. 1:10 w/v soil-to-solution ratio (20 g of soil mixed with 200 ml of DI), mixed by a reciprocating shaker for 18 hours. Long water retention time with high water content.

EC3. 1:3 w/v soil-to-solution ratio (50g of soil mixed with 150 ml of DI), mixed by a reciprocating shaker for 18 hours. Long water retention time with low water content.

After extraction, soil extractants were filtered by a 0.4 μm glass fiber filter precombusted at 400 $^{\circ}\text{C}$ for 4 hours. For every soil sample, same extraction and filtration procedures were repeated three times to make three replicates. Extractants of EC1 and EC2 then were stored in polyethylene bottles, while extractants of EC3 were stored in glass bottles for further carbon isotope analysis. Every sample was stored at 4 $^{\circ}\text{C}$.

2.2.3. Carbon isotope analysis

The analysis of $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of organic carbon was conducted to compare the properties of extracted DOC between the two tree species and across different soil depths. Stable carbon isotope, ^{13}C , can indicate the type of plant from which organic carbon is produced (Oleary 1988). Radiocarbon dating, or ^{14}C analysis, is a method to measure the age of organic matters. The ^{14}C is a radioactive isotope with a half-life of 5,730 years. The proportion of ^{14}C is expressed as $\Delta^{14}\text{C}$, which denotes the amount of ^{14}C

compared to that of standard material.

For radiocarbon analysis, soil extractants by EC3 of same soil depths were composited. Then, the radiocarbon age of extracted DOC was measured by following the established method (Raymond and Bauer 2001). The DOC samples (extracted soil solution) were firstly oxidized by high-energy (2,400 W) ultraviolet for 4 hours, converting it to CO₂, at the Biogeochemistry Lab of Seoul National University. Then, CO₂ gas was cryogenically purified using liquid N₂ in a vacuum line and sealed in a pyrex tube. After the pretreatment, the CO₂ in a pyrex tube was sent to the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS), Woods Hole Oceanographic Institution in the United States for carbon isotope analysis.

2.2.4. Chemical analysis

Concentration of DOC was measured by Shimadzu TOC-5500 (Shimadzu corporation, Japan). SOC content was determined by SSM5000A (Shimadzu corporation, Japan), in order to compare with the concentration of extracted DOC. Before the measurement, soil was air-dried to remove moisture, went through fumigation by hydrochloric acid in desiccator for 6 hours to remove inorganic carbon, and was dried for 2 hours at 60 °C (Komada et al. 2008). The concentrations of DOC and the amount of SOC were both calculated by the calibration curve method.

ICS-1600 (Dionex, Sunnyvale, CA, USA) was used to estimate the concentration of major cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺).

2.2.5. Optical analysis

UV absorbance spectrum of DOC was obtained by an ultraviolet-visible spectroscopy (Agilent technologies, Santa Clara, CA, USA) using a 1 cm quartz cell. Samples stored at 4 °C were used after their temperature

was close to the room temperature. The baseline was calibrated by using DI. Wavelengths between 200 nm and 750 nm were measured by 1 nm intervals.

Specific ultraviolet absorbance ($SUVA_{254}$) was also calculated. $SUVA_{254}$ is a useful indicator of the contents of aromatic compounds, which absorb UV of specific wavelength (254 nm) in organic matter (Weishaar et al. 2003). $SUVA_{254}$ is calculated by dividing the UV absorbance at 254 nm (Abs_{254}) by the concentration of DOC. The unit of $SUVA_{254}$ is $L\ mg^{-1}\ m^{-1}$.

2.2.6. Fluorescence analysis

Emission-excitation matrix (EEM) was determined by a fluorescence spectroscopy (Agilent technologies, Santa Clara, CA, USA). EEM is used to classify humification level of colored dissolved organic matter (CDOM), which indicate the potential sources of DOC (Coble et al. 1990, Green and Blough 1994, Stedmon et al. 2003). The EEM data was collected by measuring fluorescence spectrum of emission wave between 300 nm and 600 nm with 2 nm interval, and excitation wave between 240 nm and 450 nm with 5 nm interval. Fluorescence spectrum was standardized to Raman unit (nm^{-1}) by using the area from Raman spectrum at the excitation wave of 350 nm. Standardized spectrum was then subtracted by fluorescence spectrum of DI measured in the same day, which was also standardized to the Raman unit.

Based on the EEM, humification index (HIX) and biological index (BIX) were obtained. FI was calculated by dividing the fluorescence intensity (I) of the emission wave of 370 nm at the excitation wavelength of 450 nm by that at the excitation wavelength of 500 nm ($I_{(370:450)}/I_{(370:500)}$). HIX was obtained by the ratio of the sum of fluorescence intensity of emission wave (I) between 435-480 nm to the sum of fluorescence intensity between 300-345 nm at the excitation wavelength of 255 nm ($I_{435-480}/I_{300-345}$). BIX was obtained by dividing fluorescence intensity of the emission wave

of 310 nm by that of 430 nm at the excitation wave of 310 nm (I_{380}/I_{430}). These indices can represent the degree of humification and recent autochthonous contribution respectively (Huguet et al. 2009, Zhang et al. 2010).

2.3. Statistical analysis

To analyze the differences in the extracted amount of DOC, its properties, and the concentration of major ions under different conditions (soil depths, ECs, and tree species) one-way analysis of variance and Tukey's test were conducted. The results of these analyses were then interpreted to examine the potential impact of tree species on the properties of extracted soil solution. The differences were considered statistically significant at $p < 0.05$. Every statistical analysis was conducted using R 3.6.0.

3. Results

3.1. DOC

The concentration of water extracted soil DOC ([DOC]) was larger under *Cryptomeria japonica* than under *Quercus acutissima* on average at EC2 and EC3, but not at EC1 (Fig. 2a). Under *Cryptomeria japonica*, [DOC] of 10-30 and 30-50 cm soils were 0.3-0.5 and 0.2-0.3 mg L⁻¹ by EC1, 1.0-2.2 and 0.4-1.7 mg L⁻¹ by EC2, and 2.8-8.4 and 1.4-5.9 mg L⁻¹ by EC3, respectively. These values were significantly lower than those of 0-10 cm soil, which ranged between 0.9-1.3, 4.8-7.9, and 9.8-19.5 mg L⁻¹ at EC1, EC2 and EC3 (Table 2).

For [DOC] from *Quercus acutissima* soils, significant differences among soil depth were observed under EC1 and EC2, but not under EC3 (Fig. 2a and Table 2). [DOC] at 0-10, 10-30, and 30-50 cm soils were 0.6-1.4, 0.3-0.4, and 0.2-0.3 mg L⁻¹ by EC1, 2.6-5.9, 0.5-1.7, and 0.2-0.3 mg L⁻¹ by EC2, and 4.7-13.5, 1.3-2.9, and 0.8-3.0 mg L⁻¹ by EC3.

The optical properties of DOC were not significantly different between tree species or across soil depths (Fig. 2 and Table 2). HIX and BIX, which were each lower than 1 and higher than 1, indicate that extracted DOC could be microbially derived.

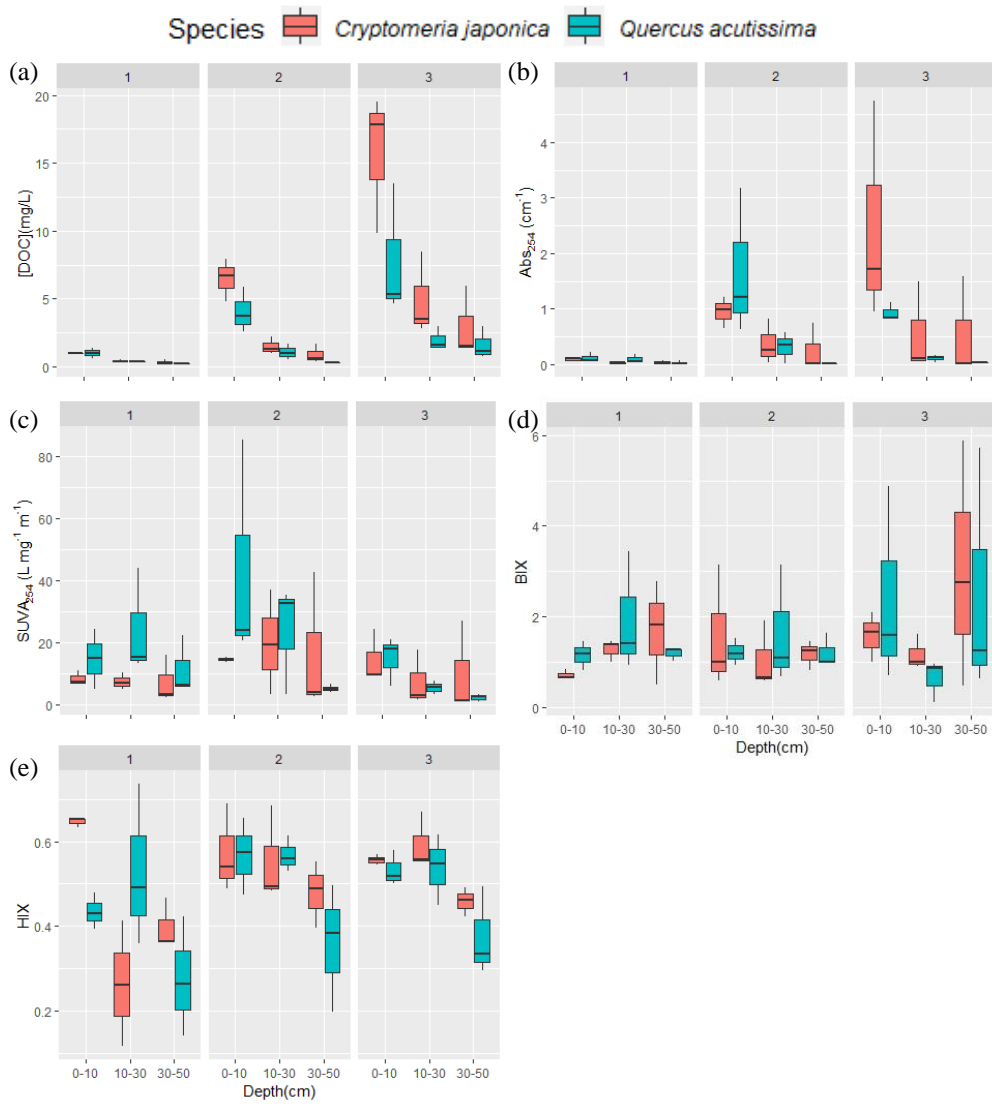


Figure 2. (a) The concentration, (b)-(c) optical properties, and (d)-(e) fluorescence indices of extracted DOC. The numbers written above each graph indicate ECs.

Table 2. The mean of the concentration, optical properties, and fluorescence indices of extracted DOC.

Tree species	EC	Soil depth (cm)	[DOC] (mg L ⁻¹)	Abs ₂₅₄ [†]	SUVA ₂₅₄ [†] (L mg ⁻¹ m ⁻¹)	BIX ^{††}	HIX ^{††}
<i>Cryptomeria japonica</i>	1	0-10	1.0 ^a	0.090	8.5	0.7	0.65 ^a
		10-30	0.4 ^b	0.030	7.5	1.3	0.26 ^b
		30-50	0.3 ^b	0.033	7.4	1.7	0.40 ^b
	2	0-10	6.51 ^a	0.95	15	1.6	0.57
		10-30	1.5 ^b	0.37	20	1.0	0.55
		30-50	0.9 ^b	0.26	17	1.2	0.48
	3	0-10	15.7 ^a	2.47	14.6	1.6	0.56
		10-30	4.9 ^b	0.55	7.5	1.2	0.59
		30-50	2.9 ^b	0.55	10.0	3.0	0.46
<i>Quercus acutissima</i>	1	0-10	1.0 ^a	0.13	15	1.2	0.44
		10-30	0.4 ^b	0.097	24	1.9	0.58
		30-50	0.2 ^b	0.030	12	1.2	0.28
	2	0-10	4.1 ^a	1.67	43.3	1.2	0.57
		10-30	1.1 ^b	0.31	23.8	1.6	0.57
		30-50	0.3 ^b	0.13	5.3	1.2	0.36
	3	0-10	7.8	0.94 ^a	15.1 ^a	2.4	0.53
		10-30	2.0	0.11 ^b	5.6 ^{ab}	0.6	0.54
		30-50	1.6	0.029 ^b	2.4 ^b	2.5	0.38

[†]Abs₂₅₄: UV absorbance at 254 nm / SUVA₂₅₄: specific ultraviolet absorbance at 254 nm

^{††}BIX: biological index / HIX: humification index

- The subscript alphabets indicate the significant difference ($p < 0.05$) across soil depths in the same EC. Tukey's test was used to find significant differences.

3.2. SOC

SOC contents in soils did not significantly vary between tree species at all soil depths (Table 3 and 4). The SOC contents in soils were 2.6-4.4, 1.4-2.7, and 0.5-1.2 % under *Cryptomeria japonica*, and 2.2-4.2, 1.4-2.7, and 0.5-1.0 % under *Quercus acutissima* at 0-10, 10-30, and 30-50 cm, respectively. Under both tree species, SOC content decreased with soil depths on average (Table 3).

Table 3. The soil organic carbon content under *Cryptomeria japonica* and *Quercus acutissima*. The values of the soil organic carbon content are expressed as mean \pm SE (standard error of mean, n=3).

Tree species	Soil depth (cm)	SOC (%)
<i>Cryptomeria japonica</i>	0-10	3.3 \pm 0.5
	10-30	2.1 \pm 0.4
	30-50	0.9 \pm 0.2
<i>Quercus acutissima</i>	0-10	3.0 \pm 0.6
	10-30	2.0 \pm 0.4
	30-50	0.8 \pm 0.2

Table 4. Statistical differences (*p*-value) of [DOC] and SOC content between *Cryptomeria japonica* and *Quercus acutissima*.

Soil depth (cm)	[DOC]			SOC
	EC1	EC2	EC3	
0-10	0.76	0.15	0.13	0.43
10-30	0.82	0.41	0.18	0.72
30-50	0.37	0.23	0.46	0.33

3.3. $\delta^{13}\text{C}$

Both $\delta^{13}\text{C}$ -DOC and $\delta^{13}\text{C}$ -SOC increased with soil depths (Table 5). In 0-10, 10-30, and 30-50 cm soils, $\delta^{13}\text{C}$ -DOC was -25.13 , -24.18 , and -23.25‰ under *Cryptomeria japonica*, and -27.08 , -26.06 , and -23.81‰ under *Quercus japonica*. At each soil depth, $\delta^{13}\text{C}$ -SOC was -25.09 , -23.46 , and -23.25‰ under *Cryptomeria japonica*, and -27.06 , -26.11 , and -24.80‰ under *Quercus acutissima*. No apparent difference in $\delta^{13}\text{C}$ of DOC and SOC between the two tree species was observed.

Table 5. $\delta^{13}\text{C}$ of extracted DOC and SOC under *Cryptomeria japonica* and *Quercus acutissima*.

Tree species	Soil depth (cm)	$\delta^{13}\text{C}$ -DOC (‰)	$\delta^{13}\text{C}$ -SOC (‰)
<i>Cryptomeria japonica</i>	0-10	-25.13	-25.09
	10-30	-24.18	-23.46
	30-50	-23.25	-23.25
<i>Quercus acutissima</i>	0-10	-27.08	-27.06
	10-30	-26.06	-26.11
	30-50	-23.81	-24.80

3.4. $\Delta^{14}\text{C}$

$\Delta^{14}\text{C}$ -DOC was 70.49, 35.08, and 4.15‰ under *Cryptomeria japonica*, and 44.90, 41.29, and -53.25‰ under *Quercus acutissima* at soil depths of 0-10, 10-30, and 30-50 cm, respectively (Table 6). ^{14}C -depleted DOC was only observed in 30-50 cm soil under *Quercus acutissima*. $\Delta^{14}\text{C}$ -DOC decreased with soil depth under both tree species.

Similar to $\Delta^{14}\text{C}$ -DOC, $\Delta^{14}\text{C}$ -SOC decreased with soil depths under both tree species (Table 6). $\Delta^{14}\text{C}$ -SOC was 54.32, -14.88, and -86.96‰ under *Cryptomeria japonica*, and 78.55, 33.80, and -73.73‰ under *Quercus acutissima* at soil depths of 0-10, 10-30, and 30-50 cm, respectively. ^{14}C -depleted SOC was found in *Cryptomeria japonica* soils of 30-50 cm and *Quercus acutissima* soils of 10-30 and 30-50 cm.

Table 6. $\Delta^{14}\text{C}$ and ^{14}C -ages of extracted DOC and SOC under *Cryptomeria japonica* and *Quercus acutissima*.

Species	Depth (cm)	$\Delta^{14}\text{C}$ -DOC (‰)	^{14}C -age (yr BP)*	$\Delta^{14}\text{C}$ -SOC (‰)	^{14}C -age (yr BP)
<i>Cryptomeria japonica</i>	0-10	70.49	Modern	54.32	Modern
	10-30	35.08	Modern	-14.88	55±20
	30-50	4.15	Modern	-86.96	665±15
<i>Quercus acutissima</i>	0-10	44.90	Modern	78.55	Modern
	10-30	41.29	Modern	33.80	Modern
	30-50	-53.25	375±20	-73.73	550±15

* “yr BP” is years before present in which present is 1950 (Stuiver and Polach 1977).

3.5. Concentrations of major cations

Significantly larger amount of cations was extracted under *Cryptomeria japonica* than under *Quercus acutissima* (Fig. 3). Under *Cryptomeria japonica*, the concentration of whole cations ([Cations]) of 0-10, 10-30, and 30-50 cm soils ranged between 99-109, 60-85, and 71-75 $\mu\text{mol}_c \text{ L}^{-1}$ by EC1, 230-330, 148-176, and 115-169 $\mu\text{mol}_c \text{ L}^{-1}$ by EC2, and 475-592, 338-382, and 284-346 $\mu\text{mol}_c \text{ L}^{-1}$ by EC3. Under *Quercus acutissima*, [Cations] of 0-10, 10-30, and 30-50 cm soils was between 67-79, 50-61, and 44-56 $\mu\text{mol}_c \text{ L}^{-1}$ by EC1, 119-203, 83-116, and 67-85 $\mu\text{mol}_c \text{ L}^{-1}$ by EC2, and 296-512, 182-273, and 135-179 $\mu\text{mol}_c \text{ L}^{-1}$ by EC3. [Cations] significantly decreased with increasing soil depths (Table 7). Though not significant, the concentration of each ion, except for Mg^{2+} , also decreased with increasing soil depth and increased with enhanced extraction conditions.

3.6. [DOC]/[Cations] ratio

In soils of *Cryptomeria japonica*, [DOC]/[Cations] ratios at 0-10, 10-30, and 30-50 cm were between 9.0-10.1, 4.7-7.12, and 2.2-7.1 $\text{mg } \mu\text{mol}_c^{-1}$ by EC1, 20.1-25.4, 6.1-14.9, and 3.5-11.6 $\text{mg } \mu\text{mol}_c^{-1}$ by EC2, and 18.1-41.0, 7.5-25, and 4.5-18.6 $\text{mg } \mu\text{mol}_c^{-1}$ by EC3. In soils of *Quercus acutissima*, the ratios at 0-10, 10-30, and 30-50 cm ranged between 8.9-19.2, 6.0-6.6, and 4.2-4.5 $\text{mg } \mu\text{mol}_c^{-1}$ by EC1, 17.9-31, 6.0-14.6, and 3.5-4.5 $\text{mg } \mu\text{mol}_c^{-1}$ by EC2, and 15.7-26.3, 7.3-10.7, and 5.6-16.7 $\text{mg } \mu\text{mol}_c^{-1}$ by EC3 (Fig. 4). [DOC]/[Cations] was not significantly different between tree species. At EC1 and EC2, [DOC]/[Cations] significantly decreased with increasing soil depth.

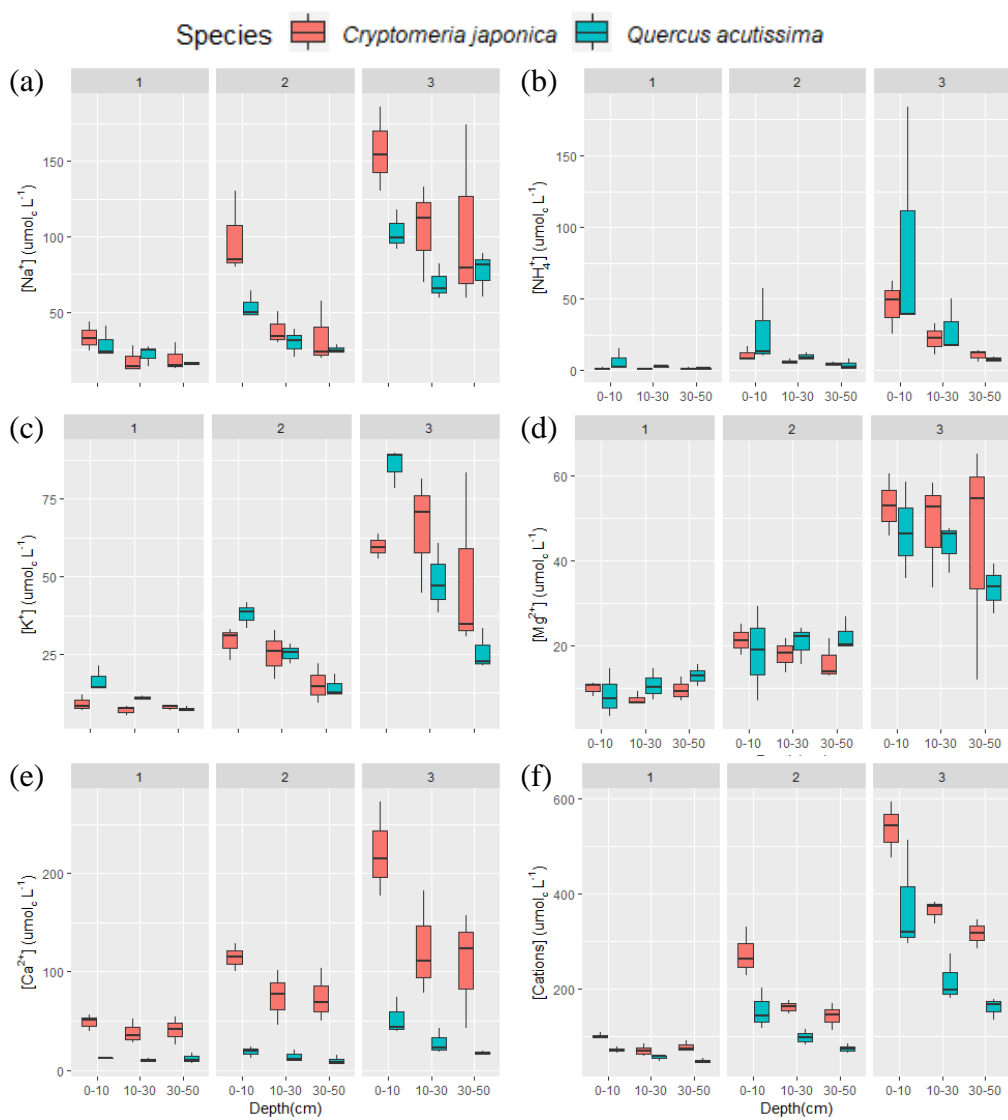


Figure 3. (a)-(e) The concentration of major cations and (f) the sum of them.

Table 7. The mean of the concentrations of major cations. The unit of the concentration is $\mu\text{mol}_c \text{ L}^{-1}$.

Tree species	EC	Soil depth (cm)	[Na ⁺]	[NH ₄ ⁺]	[K ⁺]	[Mg ²⁺]	[Ca ²⁺]	[Cations]
<i>Cryptomeria japonica</i>	1	0-10	33.6	1.3	9.1	10.0	48.7	102.6 ^a
		10-30	17.9	1.1	7.0	7.4	38.2	71.6 ^b
		30-50	19.2	1.5	8.0	9.6	40.7	79.0 ^{ab}
	2	0-10	98.4	10.8	29.0	21.4	114.7	274.4 ^a
		10-30	38.4	6.2	25.2	17.8	74.8	162.3 ^b
		30-50	33.4	4.5	15.5	16.2	73.8	143.3 ^b
	3	0-10	157.0	45.6	59.7	52.9	221.5	536.7 ^a
		10-30	105.1	22.0	65.6	48.1	123.7	364.5 ^b
		30-50	104.3	10.8	49.6	43.8	107.8	316.4 ^b
<i>Quercus acutissima</i>	1	0-10	29.2	6.8	16.7 ^a	8.4	12.1	73.2 ^a
		10-30	22.0	2.9	11.1 ^{ab}	10.7	10.4	57.1 ^b
		30-50	16.2	1.4	7.5 ^b	12.9	11.6	49.5 ^b
	2	0-10	53.9 ^a	26.9	37.8	18.5	18.8	155.9 ^a
		10-30	30.0 ^{ab}	9.7	25.3	20.7	13.9	99.6 ^{ab}
		30-50	25.2 ^b	3.9	14.6	22.2	9.7	75.6 ^b
	3	0-10	103.1 ^a	87.6	85.8	46.9	52.7	376.1 ^a
		10-30	69.2 ^b	28.3	48.7	43.6	28.2	218.1 ^{ab}
		30-50	76.9 ^{ab}	7.6	25.8	33.5	17.3	161.1 ^b

- The subscript alphabets indicate the significant difference ($p < 0.05$) across soil depths in the same EC. Tukey's test was conducted to find significant differences.

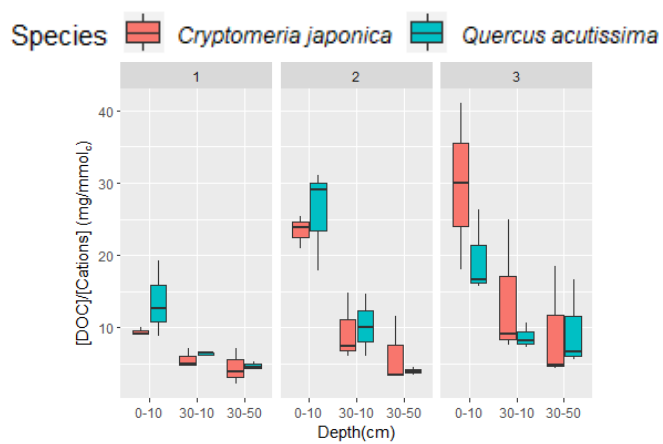


Figure 4. The ratio between [DOC] and [Cations]

4. Discussion

4.1. Concentrations of DOC and cations of extracted soil water

Though not significant, [DOC] was larger under *Cryptomeria japonica* than under *Quercus acutissima* on average at all soil depths and ECs (Fig. 2 and Table 2). This difference was in line with other studies in Europe, which reported larger [DOC] of soil solution in coniferous forest than in broadleaf forest (Currie et al. 1996, Borken et al. 2011, Fröberg et al. 2011, Camino-Serrano et al. 2014). In contrast, the difference in SOC contents was not significant between *Cryptomeria japonica* and *Quercus acutissima* (Table 3 and 4), suggesting that higher [DOC] of *Cryptomeria japonica* than that of *Quercus acutissima* was not induced by the difference in SOC contents. Rather, the result indicates that soil DOC is more hydrophilic under *Cryptomeria japonica* than under *Quercus acutissima*. The literature on the impact of aspen on SOC in North America showed that SOC under aspen was more associated with minerals and less labile than that that under conifers (Laganière et al. 2017).

Not only [DOC], but also [Cations] was larger under *Cryptomeria japonica* than under *Quercus acutissima* (Fig. 3). However, the ratio of [DOC] to [Cations], which increased with soil depth, did not vary between tree species or across ECs (Fig. 4). This suggests that [DOC]/[Cations] ratio may not be significantly influenced by tree species or hydrological condition. Such consistency of [DOC]/[Cations] ratio supported the usage of the ratio to indicate the flow path (e.g., surface runoff vs. discharge through deep soil) in which DOC is released from soil to streams. Barnes et al. (2018) showed that, in the Arctic regions and the U.S., stream DOC was originated from deep soils by using [DOC]/[Cations] ratio with $\Delta^{14}\text{C}$.

4.2. $\delta^{13}\text{C}$ - and $\Delta^{14}\text{C}$ -DOC through soil profiles

Both $\delta^{13}\text{C}$ of DOC and SOC increased with soil depth (Table 5), which aligns with other studies on $\delta^{13}\text{C}$ through soil profile (Ehleringer et al. 2000, Bostrom et al. 2007, Nakanishi et al. 2012, Brunn et al. 2014). The changes of $\delta^{13}\text{C}$ would be caused by isotopic fractionization of SOC with respiration of lighter organic carbon (Lerch et al. 2010, Werth and Kuzyakov 2010) and downward movement of hydrophilic and ^{13}C -enriched portion of organic carbon (Nakanishi et al. 2012).

Radiocarbon analysis revealed that modern DOC predominantly existed in subsoils between 0-50 cm depth, except for 30-50 cm soil under *Quercus acutissima* (Table 6). $\Delta^{14}\text{C}$ analysis on soil DOC in European and Japanese forests also reported modern DOC in soil solution around 0-20 cm soil depth (Evans et al. 2007, Fröberg et al. 2007, Don and Schulze 2008, Tipping et al. 2011, Nakanishi et al. 2012, 2014). On the other hand, DOC with negative $\Delta^{14}\text{C}$ was observed at 30-50 cm soil under *Quercus acutissima*, but not under *Cryptomeria japonica*. Other studies on $\Delta^{14}\text{C}$ of soil DOC in European forest also observed both ^{14}C -depleted and ^{14}C -enriched DOC at soil depth around 20-40 cm (Michalzik et al. 2003, Karlton et al. 2005). Since $\Delta^{14}\text{C}$ -DOC consistently decreased with increasing soil depth under both *Cryptomeria japonica* and *Quercus acutissima* in my study (Table 6), negative $\Delta^{14}\text{C}$ -DOC is highly expected at soil profile deeper than 50 cm under both tree species.

Although $\Delta^{14}\text{C}$ -SOC also decreased with soil depths, $\Delta^{14}\text{C}$ -DOC was higher than $\Delta^{14}\text{C}$ -SOC under both tree species, except for 0-10 cm soil under *Quercus acutissima* (Table 6). This result was analogous to other studies comparing $\Delta^{14}\text{C}$ -DOC and $\Delta^{14}\text{C}$ -SOC (Sanderman and Amundson 2008, Elizabeth Corbett et al. 2013, Tfaily et al. 2014). This suggests that mineral-associated organic carbon, which is a stable form of SOC and has relatively low $\Delta^{14}\text{C}$, is not likely to be the main source of extracted soil

DOC. Hydrophilic fraction of soil DOC, which can be easily exchangeable between soil water and soil particles due to weak bonds with soils (Kobayashi et al. 2012), would be the primary source of extracted DOC. This explanation can be supported by $\Delta^{14}\text{C}$ -DOC, which is between $\Delta^{14}\text{C}$ -SOC of same depth and $\Delta^{14}\text{C}$ -DOC of upper soil profile. Extracted DOC in certain soil profile could be dominated by hydrophilic DOC that had been transported from upper soil profile.

4.3. Comparison of $\Delta^{14}\text{C}$ -DOC between the two tree species

The difference of $\Delta^{14}\text{C}$ -DOC between tree species was minimal at 10-30 cm depth, but relatively large at 30-50 cm depth (Table 6), where modern and ^{14}C -depleted DOC were found under *Cryptomeria japonica* and *Quercus acutissima*, respectively. This suggests that soil DOC would be more easily translocated to deeper soil profile under *Cryptomeria japonica* than under *Quercus acutissima*. The result supports the idea that soil DOC under *Cryptomeria japonica* is more hydrophilic than that under *Quercus acutissima*, which was inferred from the variation of [DOC] between the two tree species.

Other than tree species, climatic conditions, especially precipitation, could affect $\Delta^{14}\text{C}$ of soil DOC by altering hydrology (Hentschel et al. 2009, Schulze et al. 2010, Leith et al. 2014). However, in this study, since two study sites, *Cryptomeria japonica* and *Quercus acutissima* stands, were in the same forested watershed, the difference due to the climate would be minimal. Further studies on topography or microclimate, which could affect hydrology, can elaborate the understanding the controlling factors of ^{14}C -ages of soil DOC.

5. Conclusions

In this study, soil solution was extracted from soils at varying depths under *Cryptomeria japonica*, a coniferous tree, and *Quercus acutissima*, a broadleaf tree. Through the experiment, I found that 1) ^{14}C -depleted soil DOC can be exported from mineral soils deeper than 50 cm, and 2) tree species could be the crucial factor that caused the variation of [DOC] and $\Delta^{14}\text{C}$ -DOC. The analysis on SOC supports the idea by suggesting that extracted DOC would be mainly derived from hydrophilic fraction of SOC.

However, the results need to be interpreted with caution due to the following limitations. First, since soil solution was extracted under laboratory condition, natural controls on soil DOC, such as temperature and soil moisture that can affect the concentration and properties of extracted DOC and SOC (Jones and Willett 2006, Brunn et al. 2014), were not considered. Second, this study did not cover DOC composition and structure, which can prove hydrophilicity of organic carbon (Guggenberger et al. 1994).

Despite these constraints, the findings of this study can contribute to the understanding of the carbon dynamics in subsoil in two ways. First, this study evidenced that $\Delta^{14}\text{C}$ -DOC in subsoil was not significantly different between European and Asian temperate forests. By providing the information about soil DOC in East Asia, this study could be the starting point to study the global trends of the properties and movement of soil DOC. Second, I investigated the variation of both [DOC] and $\Delta^{14}\text{C}$ -DOC that are dependent on soil depth and tree species, while the other studies focused on only one of the factors. Through the analysis, I found the potential impact of tree species on hydrophilicity of soil DOC. This study provides the data on both [DOC] and $\Delta^{14}\text{C}$ -DOC for the first time in South Korea that can be compared in the future studies to track the fates of soil DOC.

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국문 초록

용존유기탄소(DOC)는 토양에서 하천으로 유출되면 이산화탄소가 되어 대기로 배출되거나, 바다로 이동한다. 따라서 탄소순환을 이해하기 위해서는 토양 내 DOC의 양과 성질을 파악하는 것이 중요하다. 본 연구는 실험실에서의 토양수 추출 실험을 통해 두 개의 다른 수종 간 토양 DOC의 생지화학적 특성 차이를 알아보려고 하였다. 토양 시료는 전라남도 백운산 북문골에 있는 삼나무 숲과 상수리나무 숲에서 각각 토심 0-10, 10-30, 30-50 cm에서 채취하였다. 토양수는 추출 시간과 추출 농도가 다른 세 가지 추출조건에서 DI를 활용하여 추출하였다. 그 뒤 DOC와 양이온 농도, DOC의 광학특성 및 방사성 탄소 연대를 측정하였다. 측정 결과, DOC의 농도([DOC])와 양이온 농도([Cations])는 상수리나무 숲보다 삼나무 숲 토양에서 평균적으로 더 높게 나타났다. 반면, 토양유기탄소(SOC) 양은 수종 간 차이가 나타나지 않았다. 이는 SOC의 양보다 토양 DOC의 친수성이 토양 DOC 추출량에 더 큰 영향을 준다는 것을 보여준다. [DOC]와 [Cations] 비율은 수종 간 차이가 관찰되지 않았으며, 이는 [DOC]/[Cations]가 무기질 토양 내 물이 흐르는 깊이를 나타내는 지표로 활용 가능하다는 것을 의미한다. $\Delta^{14}\text{C}$ -DOC는 삼나무 숲 0-10과 10-30, 30-50 cm 토심에서 각각 70.49, 35.08, 4.15‰이었으며, 상수리나무 숲 토양에서는 각각 44.9, 41.29, -53.25‰로 측정되었다. 50 cm 이상의 토심에서는 ^{14}C 가 결핍된 DOC가 분포할 것으로 추정된다. $\Delta^{14}\text{C}$ -SOC에 비해 비교적 높은 $\Delta^{14}\text{C}$ -DOC는 토양 DOC가 토양 내 무기질에 강하게 결합한 SOC보다 친수성과 치환성이 높은 SOC로부터 유래되었을 가능성을 시사한다. 30-50 cm 토심에서 삼나무 숲의 $\Delta^{14}\text{C}$ -DOC이 상수리 나무 숲의 $\Delta^{14}\text{C}$ -DOC보다 57.40‰ 높게 나타났는데, 이는 상수리나무 숲보다 삼나무 숲에서 토양 DOC가 더 깊은 토양으로 비교적 쉽게 이동할 수 있음을 보여준다.

주요어: 용존유기탄소, 토양수, 산림유역, 수종, 방사성 탄소

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